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RESEARCH BRIEF

A SERIES OF SUMMARIES OF INFLUENTIAL RESEARCH STUDIES CONDUCTED BY CIFAR PROGRAM MEMBERS

BIO-INSPIRED SOLAR ENERGY

SOLAR CONVERSION OF CO_2 TO CO USING EARTH-ABUNDANT ELECTROCATALYSTS PREPARED BY ATOMIC LAYER MODIFICATION OF CUO

FOCUS OF STUDY:

This study focused on the use of copper oxide (CuO) nanowires coated with atomically-thin layers of tin oxide (SnO_2) to selectively convert CO_2 into carbon monoxide (CO) using only sunlight as the energy input.

BACKGROUND:

Artificial photosynthesis, or the conversion of CO_2 into carbon-based fuels and products using solar or other renewable energy sources, could at once provide a long-term energy storage solution while simultaneously stabilizing the concentration of CO_2 in the atmosphere. However, state-of-the-art catalysts that are used to convert CO_2 into useful products are usually composed of rare and precious metals, and generally lack selectivity, creating a range of products including H_2 (a by-product from water in the system), methane, methanol, ethylene, formic acid, and others

Electrode catalysts derived from copper oxide, a cheap and Earth-abundant material, were recently shown to be effective for reducing CO_2,[1] however they produced a range of products including hydrogen, carbon monoxide and formic acid. More recent reports[2,3] demonstrated that modifying the surface of these copper-based catalysts using other metals (such as tin or indium) can improve their selectivity for CO — an important chemical used in the industrial production of a wide range of products including methanol, acetic acid and liquid hydrocarbon fuels — and reduce the number of by-products. Such selective catalysts would help to improve yield and save time and cost in purification later downstream. However, creating a uniform surface coating can often be a challenge, and there is much room for improvement.

To explore this further, Michael Grätzel (École Polytechnique Fédérale de Lausanne) and a team of researchers used atomic layer deposition (ALD) to slowly deposit tin (Sn) and oxygen (O) atoms one layer at a time onto the surface of copper oxide nanowire catalysts, allowing them to control precisely how much surface material was deposited and determine how the uniform surface coating affects the activity and selectivity for the production of CO.[4] By using the modified nanowires as both the reducing electrode (for converting CO_2 into CO) and as the oxidizing electrode (for converting H_2O into oxygen gas), the research team hoped to demonstrate an efficient CO_2

1 Li CW, Kanan MW. 2012. CO_2 reduction at low overpotential on Cu electrodes resulting from the reduction of thick Cu_2O films. *J Am Chem Soc*. 134: 7231.
2 Sarfraz S et al. 2016. *Cu-Sn bimetallic catalyst for selective aqueous electroreduction of CO_2 to CO*. ACS Catal. 6: 2842-2851.
3 Rasul S et al. 2015. A highly selective copper-indium bimetallic electrocatalyst for the electrochemical reduction of aqueous CO_2 to CO. *Angew Chem Int Ed.* 54: 2146-2150.
4 Schreier M, Grätzel M et al. 2017. Solar conversion of CO_2 to CO using Earth-abundant electrocatalysts prepared by atomic layer modification of CuO. *Nat Energy*. 2: 17087.

electrolyzer that precluded the use of expensive and precious metals and provided practical advantages for construction and operation using a single material. Furthermore, by powering the electrodes using an external solar cell, the research team also hoped to prototype a functioning electrolyzer for the conversion of CO_2 to CO using only sunlight as the energy input.

STUDY DESIGN AND METHODS:

In this study, copper oxide nanowires were created by depositing copper metal onto glass and then anodizing the copper in a strongly basic solution. The resulting nanowires were then coated with SnO_2 using the ALD system, with varying treatment times and cycles to deposit different amounts of SnO_2. A series of standard characterization techniques was performed to ensure the SnO_2 had been successfully deposited. The same characterization measurements were also performed after the nanowires were subjected to extended periods of testing, in order to evaluate any changes to the structure of the wires and to ensure the SnO2 was still present after extended use.

To test the materials for their catalytic activity, the modified (CuO-SnO_2) and unmodified (CuO only) nanowires were tested and compared using an electrochemical setup (i.e. the nanowires were used as electrodes to run the reaction). Specially labeled CO_2 was used to confirm that the CO being produced was in fact originating from the CO_2 being pumped into the system, and gas adsorption measurements were used to determine how strongly carbon monoxide and hydrogen bind or stick to the surface of the catalysts, in order to better understand why the modified nanowires prefer to make CO. Finally, the nanowires were used as both the oxidizing (converting H_2O to O_2) and reducing (converting CO_2 to CO) electrodes in a bifunctional electrolyzer using a bipolar membrane (to maintain a pH gradient between electrode compartments and prevent the desired products from crossing over from one electrode to the other). This electrochemical system was connected to a triple junction gallium indium phosphide/gallium indium arsenide/germanium (GaInP/GaInAs/Ge) solar cell in order to drive the reaction using solar energy.

KEY FINDINGS:

- SnO_2 was successfully deposited onto the CuO nanowires using ALD. Standard characterization techniques confirmed the presence of SnO2 with uniform coverage across the surface of the nanowires (see Figure 1d), which is important for ensuring consistent results and maximizing efficiency.
- The unmodified (CuO only) nanowires produced a variety of products, including a large amount of hydrogen and carbon monoxide mixed with smaller amounts of methane, ethylene and ethane. The peak efficiency for CO production was found to be 36% of all products formed.
- The modified (CuO-SnO_2) nanowires produced almost exclusively CO with little hydrogen and few other side products, and performed consistently with similar activity to the unmodified nanowires. The peak efficiency/selectivity for CO conversion was found to be up to almost 90% over other products, with little loss in efficiency over several hours of operation. An ideal amount of SnO_2 was deposited after 2 ALD cycles, since any more SnO_2 caused the overall production to decrease and the selectivity for CO to decrease dramatically.

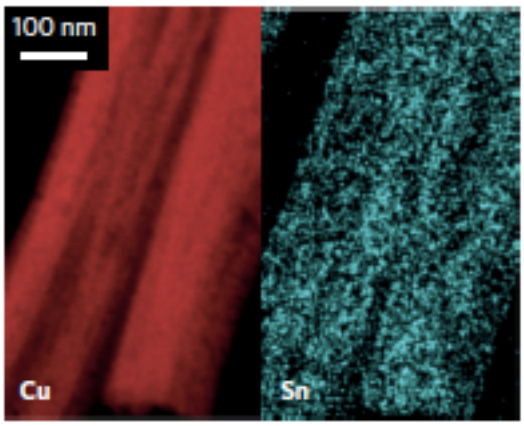

Figure 1d from the article: "Scanning transmission electron microscopy energy-dispersive X-ray mapping of a CuO nanowire after coating with five ALD cycles of SnO_2. Sn is uniformly distributed on the nanowire."

- Gas adsorption measurements confirmed that the presence of SnO2 decreased the strength of binding of hydrogen atoms to the surface of the catalysts, effectively decreasing the production of H2 on the SnO_2-modified materials and improving the selectivity for CO.
- By using the nanowires as both the reducing and oxidizing electrodes, and combining these two electrodes into one electrochemical system using a bipolar membrane to separate them, and by powering this electrochemical system with a triple junction GaInP/GaInAs/Ge solar cell, the system was able to produce CO from CO2 using only sunlight as the energy input. A record overall peak efficiency of 13.4% was achieved, with an average selectivity of 81% for CO over the course of 5 hours (see Figure 4a) and little loss in activity or efficiency.

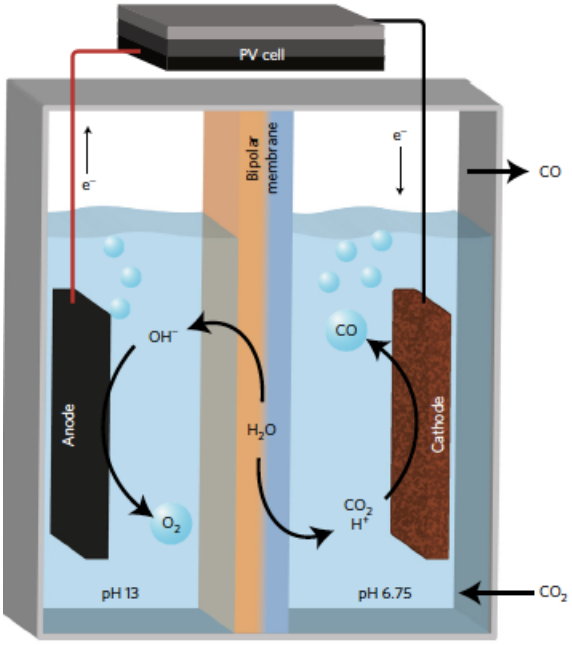

Figure 4a from the article: "Schematic of the solar-driven CO_2 reduction device. The following reactions take place. Anode: $2OH^- \rightarrow H_2O + 1/2O_2 + 2e^-$; cathode: $CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$."

CONCLUSION AND IMPLICATIONS:

This study demonstrated that ALD is an effective method for depositing uniform layers of SnO2 onto CuO nanowires for solar energy conversion applications. The atomically-thin SnO2 surface layer helped to decrease the strength of binding of hydrogen atoms to the surface of the nanowires, decreasing the production of H2 and increasing the selectivity for CO to up to ~90%. By using the modified nanowire catalysts as both the oxidizing and reducing electrodes, and using a bipolar membrane to separate them and help maintain a pH gradient, the researchers were able to demonstrate a prototype electrolyzer made of simple, Earth-abundant catalysts that can convert CO2 to CO using only sunlight as the energy input when connected to an external solar cell. The peak solar-to-CO conversion efficiency was found to be 13.4%, a new record to-date, with stable production of CO over many hours and an average selectivity for CO of 81%.

This work is an important step towards the eventual commercialization and large-scale implementation of CO2 conversion technologies, which will help not only in mitigating CO2 emissions into the atmosphere but will also help provide long-term solutions for storing excess electrical energy from the grid. The high efficiencies reported here also demonstrate the feasibility of using renewable energies to drive the transformation of CO2 into useful carbon-based products, and the high rate of production with little loss in activity over many hours of operation suggests a robustness that could one day be amenable to industrial applications. Such technologies may find important applications in industrial smokestacks (for CO2 capture and conversion), at energy production stations, or in industrial manufacturing.

REFERENCE:

Michael Grätzel (École Polytechnique Fédérale de Lausanne) is a Professor of Physical Chemistry and an Advisor to the CIFAR Program in Bio-Inspired Solar Energy. He is the lead principal investigator on this study.

RESEARCH BRIEF AUTHORSHIP:

Jonathon Moir, PhD, Research Analyst, Canadian Institute for Advanced Research (CIFAR)

CIFAR

CANADIAN INSTITUTE FOR ADVANCED RESEARCH
MaRS Centre, West Tower
661 University Ave., Suite 505
Toronto, ON M5G 1M1

www.cifar.ca